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Abstract
We report isotherm and atomic force microscopy studies of collapsed Langmuir monolayers of fatty acids. The Langmuir monolayers were overcompressed in the range 7–40 °C and transferred onto mica after the sharp pressure drop when the collapse pressure was reached. Collapsed material was observed by AFM, which revealed that the multilayers are indeed three-dimensional crystallites. We found that the shape of the crystallites depends on the collapse temperature, the phase from which the collapse occurs and/or the chain length. However, at higher temperatures the collapsed films no longer show a well defined crystallite formation, but rather a more heterogeneous melt-like pattern. We associated the crystallite formation with known bulk crystal phases of the fatty acids.

1. Introduction

Langmuir monolayers and Langmuir–Blodgett (LB) films have been the subject of intense research over the past decade as a result of the introduction of new techniques for their study, for example, fluorescence [1, 2], polarized [3, 4], Brewster angle microscopy (BAM) [5, 6] and atomic force microscopy (AFM) [7], and x-ray diffraction at grazing angles (GIXD) [8, 9]. With the aid of these techniques it has been rediscovered [10, 11] that Langmuir films show a rich polymorphism, where various phases have been shown to be two-dimensional analogues of smectic liquid crystalline phases. In addition, these films are of interest in biology as model membranes [12], and have potential application in molecular electronics [13] and the fabrication of special electrodes [14] or biosensors [15].

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However, most of the work on Langmuir films has been focused on the isotherm part where there is only a monomolecular film, from low to moderate surface pressures, about $\leqslant 35$ mN m^{-1}. Only scattered efforts have been concentrated in the last three decades on monolayer collapse. The monolayer collapse, presumably the onset of multilayer formation, is often identified in isotherm measurements as the point where the surface pressure reaches a maximum, and either a spike (a sharp pressure drop) or a plateau is observed [16]. This point is normally called the 'collapse pressure'.

Collapse has also been reported to occur at lower surface pressures, when the system is believed to be above the so-called 'equilibrium spreading pressure' (ESP) [16]. This is the pressure where the two-dimensional monolayer coexists with the bulk phase. Therefore, above the ESP all monolayers are metastable and collapse should occur as the film relaxes towards the ESP. Lundquist reported a precollapse line in acetates and esters in the middle of the so-called superliquid (LS) phase region [17]. Smith and Berg [18] studied the collapse of nine different amphiphiles by measuring the change in surface pressure versus time; they basically found that the collapse of the films was consistent with a model of homogeneous nucleation and a subsequent growth of bulk surfactant fragments. Volhardt *et al* [19], in a series of papers, have studied the kinetics of 'slow collapse' above the ESP by following the decrease in area while maintaining a constant pressure. They proposed that the collapse mechanism is in agreement with a nucleation, growth and overlap of the nucleation centres.

Direct evidence of a mechanism different from that reported for slow collapse in fatty acids above the ESP, but still much below the collapse pressure, have been reported by Galvan-Miyoshi *et al* [20]. Using BAM they observed the ejection of material in the CS phase of heneicosanoic acid through the appearance and disappearance of Airy diffraction rings.

Ries [21] studied the strong collapse of 2-hydroxytetradecanoic acid by scanning electron microscopy. He reported the formation of ridges ranging up to 200 nm in height. He proposed a collapsed mechanism where the monolayer is first weakened, then folding occurs where a double layer of molecules is pushed up. When the double layer is too long, bending occurs and finally the double layers collapses on the original monolayer. This mechanism implies that the minimum thickness of a collapsed Langmuir film is that of a triple layer of molecules. More recently, Knobler *et al* [22] have studied the same system and found that it collapses by three different mechanisms that depend on the surface pressure or the compression rate; at low surface pressures the monolayer undergoes 'slow collapse', at low compression rates 'giant folds' form in the subphase, and at higher compression rates 'multiple folds' are formed towards the air. These mechanisms were found to be reversible.

Lipp *et al* [23] studied the collapse of the coexistence of the so-called liquid condensed (LC) and solid (S) phases surrounded by a continuous liquid expanded (LE) phase in various phospholipids and in their mixtures with proteins found in lung surfactants. They showed that at the collapse pressure, there is large amplitude buckling into the water subphase. In addition, they propose that for these systems, collapse from the ordered LC or S phases occurs by fracture, while from the LE phase it occurs by loss of material either by molecular solubility or the formation of aggregates such as vesicles or liposomes.

Not only the collapse of small amphiphiles molecules has been studied but also the collapse of large macromolecules. An interesting case is the collapse of polysiloxane films at the air/water interface. It has been found that isotherms show the formations of up to seven different plateaux. Godovski *et al* [24] has shown that these plateaux correspond to a smooth collapse where a new layer is formed at each plateau. The initial growth of the second layer begins with the nucleation of three-dimensional islands, which spread in the form of ribbons, and so on.

From the theoretical standpoint, models for monolayer collapse by nucleation and growth [18, 19] and nucleation-growth collision have been proposed [19]. These theories

consider the nucleation and growth, and further overlapping of growing centres as the monolayer relaxes towards the equilibrium spreading pressure. From the microscopic understanding of collapse, it has been proposed that bulk nucleation proceeds only if defects are present [25, 26] and the growth of a solid phase is associated with a plastic deformation.

The study of the onset of multilayer formation can be important because it can give us clues to the mechanism of formation of model flat membranes from Langmuir films, and on its stability both at air/water and air/solid interfaces. In general, we can say that at the collapse pressure there is a direct and strong formation of multilayers, while collapse just above the ESP could be thought of as a progressive and slower process for multilayer formation. However, a detailed study of the three-dimensional crystallite shape and microstructures formed during collapse is still missing.

In this work we report studies of the fracture collapse of stearic, arachidic and behenic acid Langmuir films. Collapse was performed by isotherm measurements up to the collapse pressure while the monolayer was continuously compressed. After the sharp pressure drop due to collapse the films were transferred onto mica, and the shapes and sizes of the collapsed crystallites structure were observed by atomic force microscopy. Different crystallite patterns were found that depend on the collapse temperature, the phase from which the collapse occurs and/or chain length.

2. Experimental details

Stearic, arachidic and behenic acids (>99% purity) were purchased from Nu-Check (NU-Check, Oregon, USA). All acids were used without further purification. Chloroform (HPLC grade, 99.9%, Sigma-Aldrich, USA) was used as spreading and cleaning solvent. The subphase in all cases was pure water (bioresearch grade water, 18.3 MΩ cm resistivity, Nanopure, Barnstead/Thermolyne, Dubuque, Iowa, USA). The pH of the subphase was adjusted to 2, using HCl (Merck, Darmstadt, Germany). The pH was checked before each isotherm was taken.

Isotherms were obtained on a computerized Nima Langmuir–Blodgett trough (Model 622, Nima Technology LTD, Coventry, England) using a Wilhelmy plate to measure the surface pressure. To reduce contamination from dust, the trough was cover by a Plexiglas cover during isotherm measurements. The temperature of the trough was kept constant with the aid of a water circulator bath. We measured the temperature of the subphase with an Omega thermometer (Stamford, CT, USA) covered with a Teflon tube, during each isotherm measurement. The subphase temperature was found constant within a precision of 0.1 K.

The water surface was aspirated with a Pasteur pipette before the deposition of each sample, and the surface pressure was monitored with the barriers fully expanded and fully compressed. The samples were deposited on the acidified water subphase until the pressure readings were zero at the working temperature. The sample was deposited drop by drop around the surface area of the subphase, using a 100 μl Hamilton syringe, until we reached the desired initial area per molecule, about 60 Å^2/molecule. At low to moderate temperatures we waited at least 25 min to allow for the evaporation of the spreading solvent (chloroform) before compressing the monolayer. At high temperatures (>38 °C) we waited about 10 min before compressing. The isotherms were obtained by compressing the monolayer continuously at a rate of 3–5 Å^2/(molecule min). No dependence of the isotherm shape was found in this range of rate compressions.

The collapsed films were transfer onto mica by vertical dipping, in the upstroke mode, after the sharp surface drop when reaching the collapse pressure. The rate of transfer was set to 1 mm min^{-1} and freshly cleaved mica was used in all experiments. The transferred films were
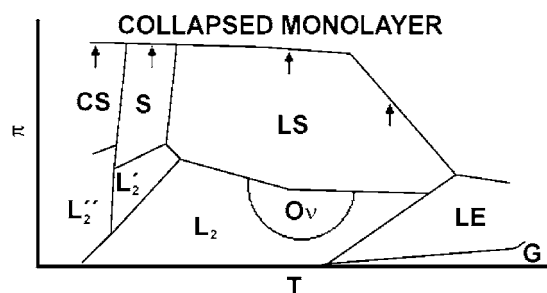
Figure 1. Schematic representation of a general phase diagram for fatty acid Langmuir monolayers (adapted from [16]). The arrows show the intended phases from which collapse should occur.

then taken to the atomic force microscope (AFM, Nanoscope IIIa, Digital Instruments, USA) for observation. We used both tapping and contact modes, and standard silicon nitride tips with a normal spring constant of 0.05 N m^{-1}. Measurements were performed with a 100 μm scanner. With the exception of flattening in some images, they have not been enhanced.

3. Results and discussion

Figure 1 shows an schematic two-dimensional phase diagram for long-chain fatty acids. It is now well known [27] that the phase diagram is shifted about 5°–6° towards higher temperatures per additional carbon in the chain. Thus the arrows show the intended regions from which collapse should occur on the fatty acids studied. Table 1, shows the temperatures at which each monolayer of the fatty acids studied were taken up to collapse; collapse was studied in the temperature range 7–40 °C. In addition, the phase from which collapse occurred is shown [16, 27]. Fatty acids can collapse from the CS, S and LS phases, which are phases where the molecules are untilted with respect to the water surface. The CS phase is a true two-dimensional crystal with a disturbed hexagonal herringbone packing with quasi-long-range positional order. The S has a centred rectangular packing of untilted molecules and the LS phase is believed to have hexatic order, i.e. short-range positional order and quasi-long-range orientational order. For a review of the phases we refer the reader to [16].

3.1. Isotherms

Figure 2 shows a series of typical isotherms for the even-chain fatty acids studied. Figure 2(a), shows the isotherms for stearic acid at 7, 21, 34 and 40 °C. At relatively large areas per molecule all isotherms show a negligible surface pressure at all temperatures; at these regions the gas phase (G) is present and coexists with a more condensed LC phase. We used the term LC as a general name to denote any phase different from the liquid expanded (LE) and G phases. Further compression raises the surface pressure as the monolayer is pushed into the pure LC phase, up to the main transition signalled by a kink in the isotherms, in the range 20–23 mN m^{-1}, although other subtle phase transitions occur before or after the main transition. Here we denote as a main transition the phase transition between tilted and untilted LC phases [16]. However, it is not the purpose of this work to review these phase transitions, which have been extensively studied before, and we will focus on the collapsed crystallite structures. In this range of temperatures all stearic acid monolayers collapse from the LS phase only [27]. The collapse pressure decreased with temperature; at the lower temperatures collapse occurs in the range 55–63 mN m^{-1}, while at the higher temperatures it decreases to about 40–45 mN m^{-1}. In this range of temperatures the liquid expanded (LE) phase is not present, indicating that we are below the LC–LE–G triple point.
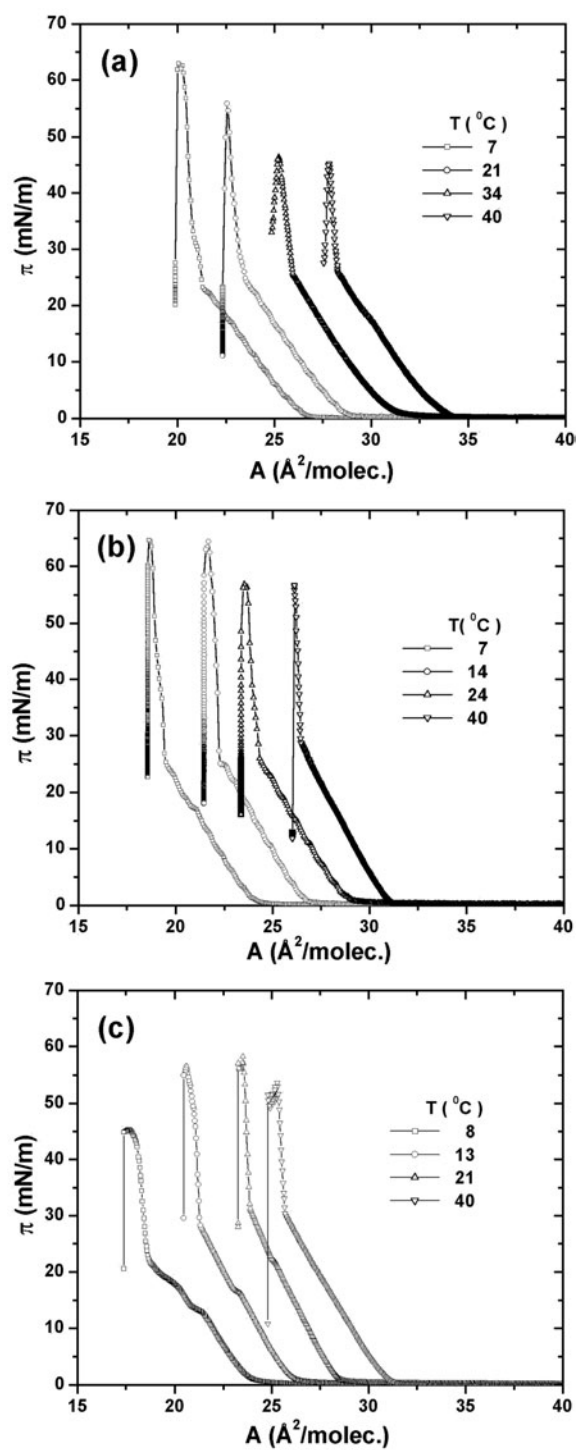
Figure 2. Surface pressure versus area (π versus A) isotherms of the three fatty acids studied taken up to collapse, which is marked by the sharp drop in surface pressure. (a) Stearic acid, (b) arachidic acid and (c) behenic acid. The isotherms were shifted to the right for clarity.

Table 1. Collapse temperatures and phases from which collapse occurred on each of the samples, averaged angles and heights, and proposed three-dimensional phase for the crystallites.

Fatty acid	Collapse temperature (°C)	Collapse form phase	Average angles of crystallites	Average height (nm)	Suggested 3D crystallite form
Stearic Acid	7	LS	117 ± 1.8 114 ± 1.3 53	21.4 ± 2.2	C
	21	LS	118.7 ± 1.2 114.5 ± 1.2 —	18.6 ± 7	C
	34	LS	119.7 ± 1.3 113.8 ± 0.3 54.8 ± 1.4	25.6 ± 8.2	C
	40	LS	—	30.8 ± 5.3	—
Arachidic acid	7	S	104.3 ± 2.0 71.3 ± 4.0 53.6 ± 1.8 128.1 ± 5.5	14 ± 3.6	B
	14	S	100.8 ± 7.0 74.7 ± 2.5 55 ± 3.2 65.7 ± 1.2 127.3 ± 6.2	23.6 ± 13	B
	24	LS	106 ± 3.6 73.5 ± 2.6 54.5 ± 2.1	11.7 ± 4.5	B
	40	LS	—	19.9 ± 7.1	—
Behenic acid	8	CS	108.2 ± 2.6 71.7 ± 2.2	12.5 ± 4	B
	13	CS	107 ± 3.6 72.5 ± 3.4	15 ± 3.5	B
	21	S	107 ± 4.7 69.1 ± 7.9	14 ± 3.6	B
	40	LS	—	12.6 ± 5.9	—

Figure 2(b) shows the isotherms of arachidic acid taken at 7, 14, 24 and 40 °C up to the collapse pressure. Again, all the isotherms start at a very low surface pressure values, indicating a coexistence between the gas and a LC phase. As in stearic acid, the LE phase is not present in the whole range of temperatures studied. The main transition occurs at about 25 mN m^{-1}, although other transitions can be noticed by the change in the isotherms slope. Here, the collapse pressure is quite similar in the whole range of temperatures studied; collapse occurs in the range of 57–65 mN m^{-1}. At 7 and 14 °C arachidic acid collapses from the S phase and it collapses from the LS phase at the other temperatures [27].

Behenic acid was studied at 8, 13, 21 and 40 °C, and figure 2(c) shows its isotherms obtained at these temperatures. The LE phase is not present in this range of temperatures. At the two lower temperatures some phase transitions are denoted clearly by changes in the isotherm slope before the main transition, which occurs at about 25 mN m^{-1}. No clear phase
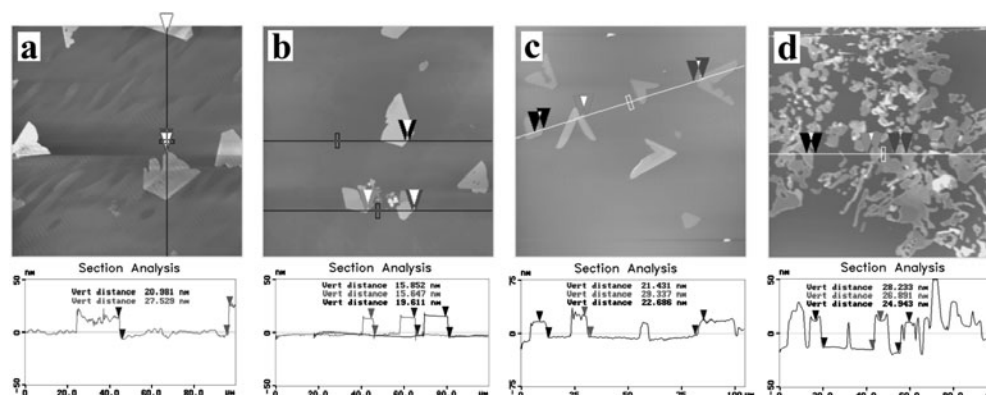
Figure 3. AFM images of crystallites obtained from collapsed stearic acid monolayers at the different temperatures studied. (a) at 7 °C, (b) at 21 °C, (c) at 34 °C and (d) at 40 °C. A height profile along the line or lines on each image is shown (section analysis).

transitions were detected at higher surface pressure. The collapse pressure is scattered within the range 45–57 mN m^{-1}. Behenic acid collapses from the CS phase at 8 and 13 °C, from the S phase at 21 °C and from the LS phase at 40 °C [27].

In general, isotherms can show two shapes at the collapse pressure, Π_c spikes or plateaux. Spikes are present when the monolayer collapses from the C, CS or LS phase. Plateaux normally appear when the monolayer collapses from the LE phase. Since in all three samples the LE phase is absent in the range of temperatures studied, we did not observe a plateau formation at collapse. However, the shape of the isotherms at the collapse pressure can also depend on the rate of compression; that is, spikes appear normally at slow rates while plateaux appear at high rates of compression [28]. At the compression rates that we used, we did not observe any dependence on the shape of the isotherms at the collapse pressure.

3.2. Stearic acid

Crystal-like structures were observed by AFM as shown in figure 3. The crystallites show definite angles averaging 117°, 114° and 53° at the lower temperatures. At the higher temperature the three-dimensional collapse material looks more like melted crystallites. The height of these structures at the three lower temperatures is not large, in the range of 20–30 nm, increasing in some cases to more than 50 nm at 40 °C. The crystallites obtained at 7 °C show some roughness, but those obtained at 14 and 34 °C are quite flat and homogeneous in height. At 40 °C the melt-like structure is quite flat but differences in height are pronounced. At all temperatures the crystallites are fragile since they can get damaged by the AFM tip during scanning, even in tapping mode.

The crystallite shape resembles a 'boomerang' at 34 °C (see figure 3(c)), and we believe the crystallites at the lower temperatures would also develop into similar structures, but they tend to be bigger and they do not have enough collapsed material to develop further, but the shapes of the crystals at the lower temperatures resemble parts of the boomerangs at 34 °C. Similar results were obtained by Neuman [29] several years ago. Using electron microscope techniques (SEM), he reported that the acute angle between the adjacent edges of the boomerang crystallites was 56°, corresponding to the crystalline C-form of stearic acid [31]. The average height he reported for this structure was 200 nm. We measured the acute angle and the height of several of the boomerang crystallites and we found an average angle of
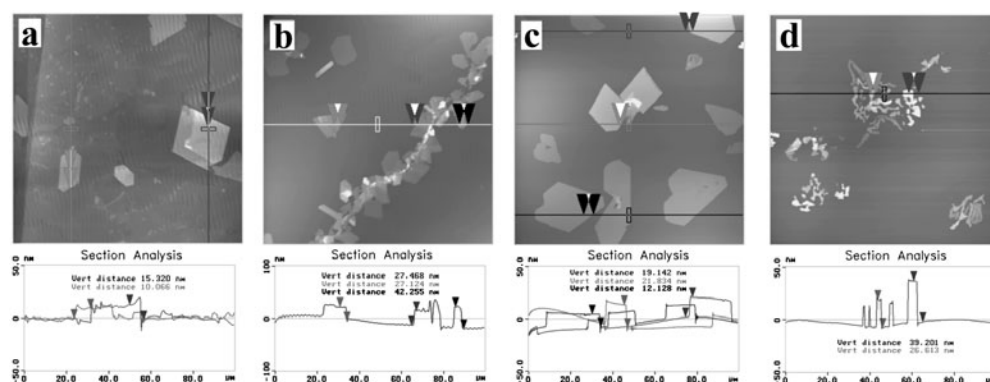
Figure 4. AFM images of crystallites obtained from collapsed arachidic acid monolayers at the different temperatures studied. (a) at 7 °C, (b) at 14 °C, (c) at 24 °C and (d) at 39 °C. A height profile along the line or lines on each image is shown (section analysis).

54.8° and none of the crystallites have a height bigger than 40 nm. We believe that Newman overestimated the height of these crystallite structures from his SEM images.

The angles formed by the macroscopic three-dimensional crystallites are related to the crystalline forms [25]. Stearic acid can form three types of three-dimensional crystal, they are called A-, B- and C-form [31]. The bilayer repeat periods for these forms are 4.64, 4.40 and 3.97 nm, respectively. Having in mind that it is energetically more favourable for the crystallites to have the upper layer with the alkyl chains towards the hydrophobic air, they must have an odd number of layers where the precursor Langmuir monolayer is also being considered, which must have the hydrophilic acid group towards the mica surface. Although we carefully tried to measure the height of the crystallites or steps at the top on their flatter part, they present a significant roughness that does not allow us to make a quantitative measurement. However, at the qualitative level we found their height is consistent with an odd number of layers if they are in the C-form at 7, 21 and 34 °C. A summary of the average angles, heights and proposed three-dimensional phase of the crystallites is shown in table 1.

3.3. Arachidic acid

According to the phase diagram obtained by Peterson *et al* [27, 30] arachidic acid collapses in the S phase at 7 and 14 °C and in the LS phase at 24 and 40 °C. Crystallite structures were found at the three lower temperatures while at 40 °C they resemble a melted structure, yet the crystallites are very large and with straight and sharp boundaries as shown in figure 4. Figure 4(a) shows isolated crystals, which are likely to form when collapse occurs at point defects, e.g. vacancies and/or dislocations. However, we found that collapse from the S phase, this is at the two lower temperatures, tends to produce crystallites that are mostly aggregated in aligned structures, along what seem to be defect lines or boundaries between domains. A remarkable aggregation of crystallites aligned along a defect line is shown in figure 4(b), but isolated crystallites could also be found (see also figure 4(a)).

At the two higher temperatures the crystallites tend to appear randomly and isolated. This might reflect that the density of line defects is much higher in the S phase than in the LS phase since in stearic acid, which collapses from the latter LS, we only observed the formation of isolated crystallite structures. It indicates that the ordering of the phase from which collapse occurs is important. That is, the S phase has a distorted hexagonal packing, i.e. centred rectangular packing, with quasi-long range orientational order where domains will not have
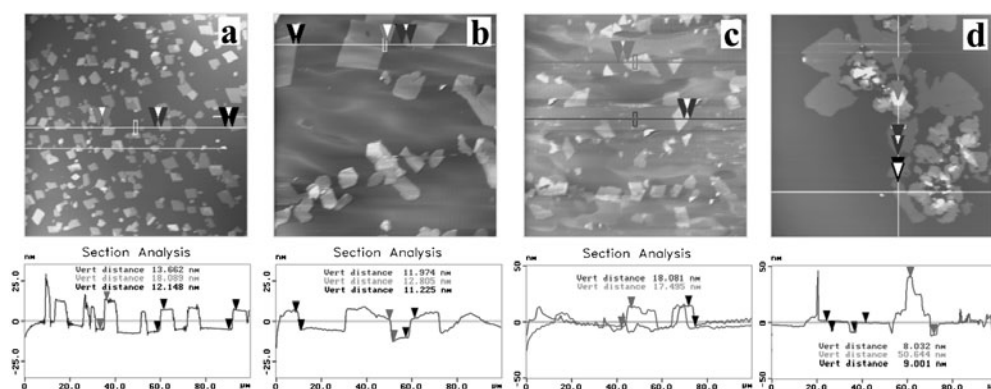
Figure 5. AFM images of the crystallites obtained from collapsed behenic acid monolayers at the different temperatures studied: (a) at 8 °C, (b) at 13 °C, (c) at 21 °C and (d) at 40 °C. A height profile along the line or lines on each image is shown (section analysis).

enough time to heal their mismatch in orientation, leaving a large density of line defects, and inherent point defects as well. The superliquid LS phase has a hexatic ordering and it is a phase of low viscosity, thus line defects could heal and point defects are likely to survive during compression; therefore, the monolayer will have higher energy at these points and collapse is likely to occur at these defects, resulting in the formation of isolated crystallites.

We measured three different average angles on most of the crystallites at the three lower temperature, their values are around 104°, 77° and 54°. Only the smaller angle is similar to one found in stearic acid. It can be observed in table 1 that at 7° and 14° we measured four and five different angles, respectively, which might also indicate growth in two different directions. These could also be taken as an indication of a different 3D crystallite form from the C-form reported for stearic acid. However, a few crystals show angles similar to those found in stearic acid. Arachidic acid presents only the B and C three-dimensional crystal forms [31], which have a repeating distance for a bilayer of 4.84 and 4.41 nm, respectively. We carefully measure the height of the crystallites of arachidic acid, looking for the flatter parts and the smaller steps at the top of the crystallites. We found that an odd number of layers is consistent with a repeating distance of 4.84 nm. Thus, given that the angles obtained are different from those of the C-form of stearic acid and a consistency of 4.84 nm for a bilayer, we suggest that arachidic acid forms the three-dimensional B-crystalline form. This finding is in agreement with that obtained by grazing incidence x-ray diffraction performed *in situ* at the air/water interface [32].

3.4. Behenic acid

This acid collapses in the condensed solid phase, CS, at 8 °C, from the solid phase, S, at 13 and 21 °C and in the super liquid, LS, phase at 40 °C [27, 30]. Images of transferred LB films at these temperatures were obtained as shown in figure 5. At 8 °C, this acid collapses forming isolated or linearly aligned crystallites with a similar density, suggesting that the collapse occurs both at line defects and at point defects in the CS phase. Figure 5(a) shows a typical image of isolated crystallites at this temperature, the linearly aligned crystallites with similar shapes will be presented elsewhere [33]. The average area size of the crystallites formed during collapse are not as big as in the case of stearic and arachidic acid. An almost homogeneous height distribution is observed around 13.1 nm. The average area size of the crystals is rather small, about 15 μm^2.

Collapse from the S phase at 13 and 21 °C shows linearly aligned and isolated crystallites, as shown in figures 5(b) and (c). These crystallites are much bigger than those formed at 8 °C. At 40 °C the collapsed material resembles again a melt, but some edges are very sharp.

In general, the behenic acid crystallites have a rhomboidal shape with very sharp edges. The two average angles of the crystals that define the parallelograms were measured giving values of about 107° and 72°, as shown in table 1. These angles are not very different with temperature. In addition, they are different from the ones obtained for stearic acid but close to two of the angles found for arachidic acid. Behenic acid is known to have the B- and C-crystalline forms in bulk [31]. The repeat periods of the bilayers in bulk are 5.30 and 4.83 nm, respectively. The thicknesses measured of the steps and of the full crystallite height are consistent with an even (steps) or odd number of layers (crystallites) if the repeat period is 5.3 nm. Suggesting that in this range of temperatures behenic acid forms only the B-form.

4. Conclusions

We present a study on the shape, size and patterns formed by the even-chain stearic, arachidic and behenic fatty acids during monolayer collapse. In the range of temperatures studied, the monolayers formed by these fatty acids collapse from the different phases known as CS, S and LS. The range of temperatures selected for the collapse of monolayers of stearic acid were chosen so it collapses from the LS phase only. In the case of arachidic acid, collapse of its monolayers occurred from the S and LS phases. For behenic acid collapse occurred from the CS, S and LS phases.

Our results show that defects present in the precursor monolayer phase are important in the morphology of the collapsed crystallite aggregates. That is, for crystallites formed from the collapse of the CS phase, linearly aligned and isolated 3D crystallites are observed. Collapse from the S phase produce mostly linearly aligned crystallites and fewer isolated crystallites. Collapse from the LS phase produced isolated crystallites only. These results are consistent with the nature of each monolayer phase, since the CS phase is the only true 2D crystalline phase, where healing of line defects as well as of dislocations will be difficult during compression, thus matter will be expelled to the third dimension from both types of defect. The S monolayer phase has less order than the CS phase and most dislocation defects apparently heal during compression while line defects between different grain domains do not, thus mostly linearly aligned crystalline structures will be present during collapse. On the contrary, line defects in the hexatic LS phase are unlikely to appear and only point defects must be present, so only isolated crystallites are formed during collapse.

In addition, we found that the crystallites formed during collapse from the S and LS phases are much larger than those formed from the CS phase, although the density of the crystallites from the former phases is much less than the crystallite density from the latter phase. This might reflect that spreading of a fatty acid (collapsed material) on a fatty acid (monolayer) is easier when the monolayer is less ordered; that is, the spreading is easier in the LS and S phases and more difficult on the crystalline CS phase.

The shapes of the 3D crystallites are different, from rhomboidal to pointy platelets and boomerangs, and melt-like shapes at higher temperature. Crystallites also show very well defined angles, especially those formed from collapsed monolayers at low temperatures. In general we found that crystallites tend to be fragile, as they tend to be easily damaged by the AFM tip during scanning.

Typically, the crystallites formed during collapse at a given temperature tend to be quite homogeneous in height, but there is no clear dependence on the average height with the collapse temperature. Our results show the importance of defects for monolayer collapse in agreement

with theories [25], since collapse occurred at line and point defects. However, collapse from a line defect tends to form much higher crystallites at the centre of the line, about 200 nm, and shallower and rather flat crystallites away from it, while collapse at point defects forms shallower crystallites. At 40 °C, the collapse material resembles a melt where large and tall crystallites, greater than 50 nm, can be observed.

Acknowledgments

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